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Solvational Barriers to Interfacial Electron Transfer:

Minimization via Valence Delocalization

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13. ABSTRACT (Maximum 200 words) <p><i>Abstract:</i> Standard rate constants (k_s) for interfacial electron transfer (ET) have been obtained for several redox couples featuring very small internal activation barriers. To render these ordinarily fast rates measurable, we have employed low-defect-density, highly ordered pyrolytic graphite (HOPG) as an electrode material (see: Allred and McCreery, <i>Anal. Chem.</i>, 1992, 64, 444). At the HOPG/aqueous solution interface, we observe - for the first time - the systematic (exponential) increase of k_s with inverse reactant size, predicted by Marcus for electrochemical reactions whose barriers are primarily defined by solvent reorganizational effects. We also observe that rates can be significantly accelerated by delocalizing electrons over multiple metal-centered trapping sites. The degree of rate acceleration is quantitatively consistent with the extent of solvent barrier lowering expected if electronic delocalization effectively increases the radius of the ET reaction site.</p>				
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Activation barriers, and therefore rates, for electron transfer (ET) at electrochemical interfaces are believed to depend strongly on solvent repolarization and reorganizational energetics.¹ Furthermore, available continuum theory² suggests that interfacial solvent barriers (ΔG_s^*) should vary in a comparatively simple and predictable way with parameters such as molecular reactant/electrode separation distance (d), reactant radius (r), optical and static solvent dielectric constants (D_{op} and D_s), and amount of charge (e) actually transferred:

$$\Delta G_s^* = (e^2/8)(1/r - 1/d)(1/D_{op} - 1/D_s) \quad (1)$$

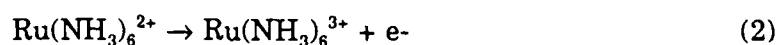
The expected behavior at interfaces, therefore, is quite similar to that in homogeneous solution.^{2,3} In contrast to ET in homogeneous solution, however, there has been remarkably little *unambiguous* documentation of solvent-related barrier effects for interfacial processes.⁴ Among the apparent experimental problems are: 1) large and variable interfacial work terms (adsorption, diffuse double layer effects, etc.) which tend to be both reactant and solvent specific, and 2) inherently inefficient one-dimensional diffusion to planar electrodes⁵ - which tends to make all but the slowest reactions kinetically inaccessible. Slow reactions, in turn, often feature large internal reorganizational barriers, spin changes, bond breakage, coordination number changes, and/or other kinetic complexities which make the identification and isolation of purely solvent related effects difficult. Nevertheless, we wish to report here the experimental observation

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of interfacial rate behavior consistent with eq. 1, where the experimental variable is the reactant size and where the reactants have been chosen so as to feature primarily solvent based activation energetics. As detailed below, one of the keys in the investigation has been the use of highly ordered pyrolytic graphite (HOPG) as an electrode material. With HOPG, we have additionally observed that solvent barriers can be significantly reduced by employing electronically delocalized reactants.

Figure 1 shows a plot of the log of the standard electrochemical rate constant (k_s) for each of a series of mononuclear and dinuclear transition-metal complexes (primarily ruthenium) versus the inverse size of the complex. The reactants in all cases are low-spin d^6 species. They were chosen, in part, because of known (or anticipated) minimal internal reorganizational requirements.^{6,7} The kinetics data plotted are actually ratios of k_s values in comparison to k_s for the slowest reaction:⁸



Rate parameters, in all cases, were determined by digital simulation⁹ and/or Nicholson analysis¹⁰ of experimental cyclic voltammograms obtained at conventional sweep rates (ca. 200 mV/s). Typical absolute rate constants for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ reaction at HOPG were ca. $1 \times 10^4 \text{ cm s}^{-1}$. In contrast, the same reaction proved immeasurably fast ($k_s > 3 \times 10^{-2} \text{ cm s}^{-1}$) at a conventional glassy

carbon electrode/aqueous solution interface.¹¹ The large rate difference is consistent with the more general observation by McCreery and co-workers of rate decreases of 4 to 5 orders of magnitude for a broad range of redox couples at low-defect-density HOPG.^{12d} While the origin of the attenuation effect is somewhat obscure (presumably it is electronic...), we (and others¹²) find that it is reproducible below a critical threshold surface defect density.¹³ In any case, rate attenuation is essential; without it, none of the targeted redox systems is kinetically accessible by the slow sweep-rate voltammetry method. A second key feature of the HOPG/aqueous interface is its extremely low capacitance¹⁴ - which translates into the buildup of negligible amounts of surface charge, even at electrode potentials far removed from the potential of zero charge (ca. - 0.2 V vs. s.c.e.¹⁴). This is tremendously advantageous because it effectively eliminates electrostatic work terms (diffuse double layer effects¹⁵) which might otherwise dominate the interfacial kinetics (especially with reactant and product charges varying from 2+ to 6+).¹⁶

Returning to Figure 1, the size parameter chosen - in light of eq. 1 - was the inverse of the reactant radius. This parameter is reasonably well defined for roughly spherical, homoleptic complexes such as $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$, but is obviously not so well defined for heteroleptic complexes - especially dinuclear complexes. For these complexes, we used an average radius defined as:

$$r_{av} = (r_x r_y r_z)^{1/3} \quad (3)$$

where x , y and z are metal-ligand bonding axes. While the averaging formula obviously is somewhat arbitrary, we note that it has been successfully used previously to correlate size-dependent metal-complex diffusion coefficients,¹⁷ redox reaction entropies,¹⁸ and homogeneous electron self-exchange rate constants.^{3a} Furthermore, in our study the two complexes with the best defined radii bracket those that require size averaging. In any case, the observed correlation is compelling: k_s increases *exponentially* with increasing reactant radius. The slope of the $\log(k_s)$ vs. r_{av}^{-1} plot is -12 \AA , or $16 \text{ kcal mol}^{-1} \text{ \AA}$ for ΔG^* vs. r_{av}^{-1} .¹⁹ Assuming, for convenience (and for lack of independent information), that d is unchanging, the expected slope from eq. 1 is $22 \text{ kcal mol}^{-1} \text{ \AA}$. Related studies^{3a} in homogeneous solution (work-corrected bimolecular self exchange) yield a slope of $45 \text{ kcal mol}^{-1} \text{ \AA}$, i.e. somewhat greater than the factor of two difference expected if d variations are again neglected.^{2,20}

Based on eq. 1, we reasoned that redox reaction site sizes could be effectively increased and solvational barriers effectively lowered by delocalizing electrons over multiple trapping sites. The central data points in Figure 1, corresponding to the stepwise oxidation of the electronically delocalized Creutz-Taube ion $((\text{NH}_3)_5\text{Ru-pyrazine-Ru}(\text{NH}_3)_5^{4+})$ and a *trans*-pyridine-substituted analog,²¹ appear to confirm the hypothesis:²² Interfacial ET rates are significantly greater for these species than for the parent mononuclear complexes. From eqs. 1 and 3, one would expect further solvent barrier diminution and further rate acceleration with larger oligomeric species. Extension and delocalization in only

one dimension (i.e. linear oligomerization) is anticipated, however, to induce only modest additional barrier lowering. For example, extension of the Creutz-Taube ion to 6 metal centers total (i.e. the largest currently known Creutz-Taube oligomer;²³ z-axis length of ~ 42 Å) should further decrease ΔG_s^* by only about 0.9 kcal mol⁻¹ (based on extrapolation of the correlation in Figure 1). A more effective strategy would appear to be to induce delocalization in a second (or even third) dimension. Selected ligand-bridged clusters would be attractive target systems.²⁴

We conclude that: 1) solvent reorganization does play a major role in defining redox reactivity at surfaces, 2) the dependence of the barrier height on molecular reactant size is reasonably well predicted by conventional dielectric continuum theory, and 3) the barrier height is susceptible to manipulation and diminution by a valence delocalization strategy.

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13. HOPG defect densities on well characterized surfaces have been correlated with a number of interesting effects or parameters.^{12a} Such effects or parameters can subsequently be used as indirect probes of defect density on less well characterized surfaces.^{12c} An indirect probe which we found both convenient and relevant was the extent of kinetic reversibility of the $\text{Fe}(\text{CN})_6^{4-/3-}$ couple (poorer reversibility corresponding to lower defect density). Following Allred and McCreery,^{12c} we adopted the criterion that

the C.V. peak separation (a measure of kinetic (ir)reversibility) exceed 700 mV before a surface could be accepted for further study.

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Figure caption

Log of k_s for the indicated ET reaction (normalized to k_s for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$) versus the inverse radius of the reactant (eq. 3). The electrode material is low-defect-density HOPG;^{12,13} the electrolyte is 1M aq. NaCl. Line drawn is a best-fit line for all points except point 6 (open circle).²¹ Key to data points:

- 1) $\text{Ru}(\text{NH}_3)_6$,
- 2) $\text{Ru}(\text{NH}_3)_5(\text{pyridine})^{3+/2+}$,
- 3) $(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5^{5+/4+}$,
- 4) $(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5^{6+/5+}$,
- 5) $t\text{-(pyridine)}(\text{NH}_3)_4\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_4(\text{pyridine})^{5+/4+}$,
- 6) $t\text{-(pyridine)}(\text{NH}_3)_4\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_4(\text{pyrazine})^{6+/5+}$, and
- 7) $\text{Fe}(\text{phenanthroline})_3^{3+/2+}$ (data for point 7 obtained from ref. 12d).